

Homogeneous and Supported Niobium Catalysts as Lewis Acid and Radical Catalysts

Dr. Wayne Tikkanen

Department of Chemistry and Biochemistry, California State University, 5151 State University Drive, Los Angeles, CA 90032

Vox: 323.343.2372

FAX: 323.343.6490

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Objectives: The objectives of this work are to train students to be proficient in work at research and development positions in energy related positions while they participate in this research project. The project will involve the synthesis and characterization of new chiral amido or alkoxide complexes of niobium where the metal is bound to either a polyarylcyclopentadienyl group or to high surface area silica gel and their testing as catalysts in several C-C bond-forming reactions. The ultimate aim is to develop catalysts that will promote important C-C bond formation reactions under mild conditions using small molecules that can be derived from coal. The processes will be atom efficient, generating a minimum of byproducts that would need to be disposed or used in other processes.

Accomplishments to Date: The testing of catalyst candidates pentaphenylcyclopentadienyl niobium(V)chloride and pentaphenylcyclopentadienyl niobium(IV)chloride was not accomplished as there were problems preparing the desired compounds. Extended study of the reaction products obtained with acetonitrile solvent revealed that the pentaphenylcyclopentadienide anion underwent two different reaction paths, depending upon order of addition. One gave pentaphenylcyclopentadiene, with a hydrogen atom abstracted from the acetonitrile solvent. The other gave the pentaphenylcyclopentadienyl *radical*. Attempts to prepare a less easily oxidized pentaphenylcyclopentadiene donor, trimethylsilylpentaphenylcyclopentadiene were unsuccessful; however the somewhat less bulky trimethylsilyltetraphenylcyclopentadiene has been prepared. We found this compound to react with niobium pentachloride, although here two reaction paths occur, giving a mixture of the trimethylsilyltetraphenylcyclopentadiene-niobium(V)chloride and tetraphenylcyclopentadiene-niobium(V)chloride which do not readily separate.

To address this problem, another precursor, trimethylsilyltetraphenylcyclopentadiene has been prepared and characterized by ^1H NMR spectroscopy. Preliminary studies indicate this tin derivative undergoes cleaner reaction with niobium pentachloride; this reaction is still being optimized.

Finally, the determination of optimal drying conditions of high surface area silica gel in preparation for the attachment of niobium complexes has been addressed using a redox stable, NMR sensitive probe, $\text{Zr}(\text{N}(\text{CH}_3)_2)_4$. Drying at 100° in vacuo for 20 hours followed by reaction with the probe in toluene results in a surface attached species with a single resonance in the CP-MAS ^{13}C NMR and a clean CP-MAS ^{29}Si NMR spectrum which shows a predominance of Q3 silicon signals. This work lays the ground work for preparing silica bound niobium complexes that can act as Lewis acid or radical catalysts.

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